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Determination of Polycyclic Aromatic Hydrocarbons in Soil and Water Around Automobile Repair Workshops within Eket Metropolis in Akwa Ibom State, Nigeria using GC-MS

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are widespread in air, water, terrestrial, and biological systems and can be transferred between these resources. Sixteen United States-Environmental Protection Agency (US-EPA) priority PAHs in soils and underground water from some automobile repair workshops within Eket metropolis in Akwa Ibom State, Nigeria were determined using gas chromatography-mass spectrometry (GC-MS) to assess the extent of pollution caused by automobile repair activities. Soil samples were collected at various depths within five automobile repair workshops using stainless steel hand-held auger. Water samples were also collected from boreholes around the vicinity of the automobile repair workshops using an amber glass bottle with a screw cap. The results obtained showed that all the sixteen US-EPA priority PAHs were detected in varying concentrations in the soil samples while dibenzo(a,h)anthracene was not detected in any of the water samples. The Σ16 EPA PAHs detected in the soil samples in the five automobile repair workshops ranged from 0.82-12.98 mg/kg. The Σ15 EPA PAHs detected in the water samples ranged from 1.71-16.07 mg/l. According to the European Commission classification system of soil contamination, the soil was classified to be moderate to heavily contaminated. The carcinogenic potency BaP equivalent concentration (BaPeq) for the soil samples ranged from 0.4610-1.5058 mg/kg. The BaPeq for the water samples around the sampling sites ranged from 0.1644-0.4238 mg/l. Diagnostic ratios showed that the possible sources of PAHs in this study area were derived from mixed sources (Pyrogenic, Petrogenic, and phytogenic sources). Hence the soils and water around the workshop are moderately contaminated.

Keywords: Polycyclic Aromatic Hydrocarbons, Automobiles repair workshops, Contamination, Soil and underground water, Gas chromatography-mass spectrometry

1 Introduction

Automobiles consist of the main basic ways of movement of individuals and materials globally. The usefulness of this way of movement is not without a price which includes pollution of various magnitudes. This price according to Halls [1] can be grouped into two; operational price and the maintenance price. When automobiles are moved from one place to another, operational price is paid whereas, during vehicle repairs, maintenance price is involved. International conferences and meetings paid more attention to the reduction of the operational price of automobile pollution by introducing alternatives such as the use of ethanol and hydrogen fuels for powering automobiles, removal of lead from gasoline, use of electric trains for urban transportation, etc. A lot of these have been put to use or interpreted into their local contents [2]. Little or no attention is paid to pollution arising from maintenance or vehicle repairs. There is a greater amount of pollution arising from the intensive operations of these automobile or auto-mechanic activities [3].

Pollution due to disposal of used engine oil is more prevalent than that of crude oil. This is a serious environmental problem in Nigeria and calls for urgent attention [4]. Contamination may result from mishandling, deliberate disposal, spilling, and leakage of petroleum products such as gasoline, lubricating oils, diesel fuel, heating oils, used and spent engine oil. These unguided practices of indiscriminate disposal have worsened the rate at which used engine oils spread and contaminate the soil and water around the town. Researches have indicated the presence of more than 600 organic compounds in the environment, the most important of which belong to the following classes: Petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), ketones, aldehydes, and alcohols [5]. Organic pollutants are brought to the atmosphere due to their volatility either through

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evaporation from the earth's surface or through emissions from human activities and can be transported over long distances. Polycyclic aromatic hydrocarbons interact to different extents with water, soil/sediments, and biota due to the different physiochemical properties of organic contaminants. The US Environmental Protection Agency (EPA) has identified the 16 most frequently occurring and/or dangerous PAHs as priority pollutants and has divided them into carcinogenic and non-carcinogenic groups [6]. The human carcinogens include Chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(a)anthracene (BaA), benzo(k)fluoranthene (BkF), dibenzo(a,h)anthracene (DbA) and indeno(123cd)pyrene (IcdP) (USEPA, 2002). Recently, Benzo(a)pyrene (BaP), one of the high molecular weight PAHs, has been classified into the group of most carcinogenic agents by the International Agency for Research on Cancer [7].

PAHs can be transferred between air, water, terrestrial and biological systems, that is leaching of PAHs from soil resources into groundwater or transport of particulate soil PAH in the atmosphere [8]. PAHs are usually persistent in the subsurface environment. That is they may be present long after contamination or pollution incidence and cannot be removed from the subsurface within a reasonable period by pump and treat technique [9]. Their low solubility often results in their accumulation in soils, sediments, and underground water. Akwa Ibom State being one of the most populated states in Nigeria has witnessed an increase in the number of vehicles used for commercial and private purposes. Vehicles being prone to breakdown, portions of land are used by individuals or groups of people for small and large scale automobile workshops to offer services to the public. It is expected that there are environmental threats associated with this practice. This has posed serious effects on human health. Hence the present study is designed to investigate the pollution status of soil and underground water around automobile workshops in the Eket Local Government Area in Akwa Ibom State.

2 Materials and methods

2.1 Study area

The study area "Eket" is the second-largest city in Akwa Ibom State, Nigeria [10]. It has a human population of 364,489 as of the 2013 projected population. Figure 1 shows the location map of the study area. The area enjoys the influence of maritime which is all year-round. The rainy season occurs between March and October with a short dry season from November to February. Eket has a mean annual rainfall of 2484 mm and a means the yearly temperature of 29 °C. It has relative humidity range of 70% -80% [11]. Eket has a stabilized ground surface that has greatly increased the rate of rainfall infiltration into the ground. In some locations, boreholes are sited near mechanic workshops with little or no consideration to the possibility of groundwater contamination through seepage.

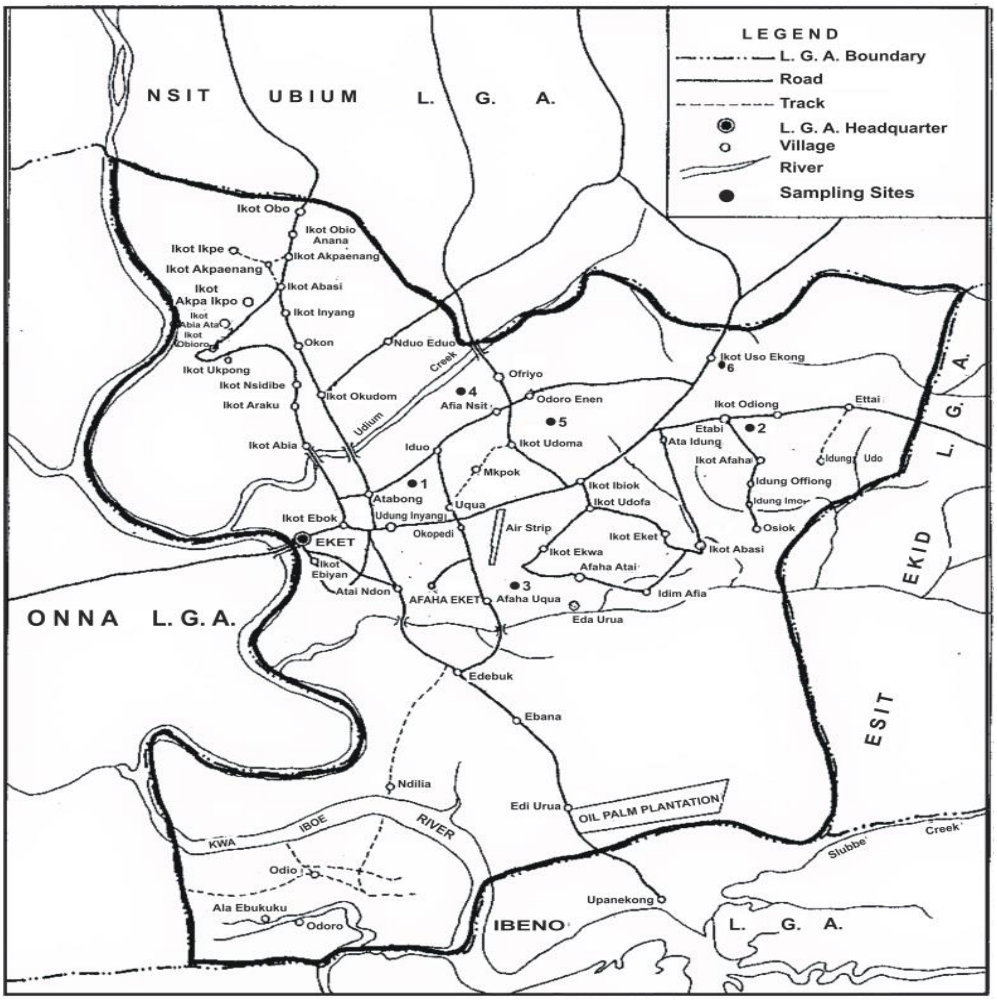

Figure 1: Map of the study area (Eket) showing the sampling sites[10]

2.2 Selection of sampling sites

Since groundwater pollution status of an area is influenced or controlled by some factors such as topographic slope, groundwater table variation, soil porosity, the permeability of the aquiferous layers, the type and quantity of waste and land use activities, five (5) automobile repair workshops were chosen within Eket metropolis and one control site namely: (1) automobile repair workshop at Nkubia Street (NK) (2) automobile repair workshop at Etebi Idung Iwak (EIW) (3) automobile repair workshop at Edem Udo Street (EU) (4) automobile repair workshop at Grace Bill road (GB) (5) automobile repair workshop at RCC road (RCC) and a control sample from Okon Primary School premises, Eket (OPS).

2.3 Standards and reagents

All chemicals used were of Analar grade and the highest purity. Reagents used include hexane, dichloromethane, alumina (GC grade) as a desiccant, concentrated H_2SO_4, anhydrous sodium sulphate, and organic-free reagent water. A standard mixture of the US EPA 16 priority PAHs purchased from Accu Standard, USA.

2.4 Sample collection

Soil samples were collected at different points (using random sampling method) in each of the automobile repair workshops between April - June. Soil samples were collected in three sets with a stainless handheld auger. One set which was the top layer was between 0 – 10 cm from the surface, the second set which was the middle layer was collected between 10-20 cm below the surface, the third set which was the bottom layer was collected below the surface at depth of 20-30 cm. The replicate samples collected at each point were thoroughly mixed to form one composite sample. A control sample was also taken following the same procedure from a serene environment. The samples were wrapped in aluminum foil and preserved in the laboratory until extraction and analysis. Water samples were also collected from residential areas (not beyond 150m away from Automobile Repair Workshops) around the vicinity of the five(5) mechanic workshops between April - June between and stored in precleaned labeled 1-liter amber glass bottles fitted with screw caps in the laboratory. A control sample was also taken following the same procedure from a serene environment. It was preserved in an ice chest at 4°C until analysis.

2.5 Sample preparation and treatment

2.5.1 Extraction

2.5.1.1 Soil samples

The soil samples were air-dried in a dust-free environment at room temperature before the extraction for PAHs analysis. The soil samples were pulverized with a porcelain mortar and pestle and sieved through a 2 mm mesh size sieve. The extraction of PAHs from the samples was reported elsewhere [10]. Briefly, to avoid contamination, all glassware was cleaned with soap and water, rinsed with distilled water, and finally rinsed with hexane and dichloromethane (3:1) mixture. Soil samples (10 g) were extracted with hexane and dichloromethane (3:1, 200 ml) in a soxhlet extractor for 16-24 hours at 4-6 cycles/hour depending on the sample.

2.5.1.2 Water samples

Before the extraction, the sample bottles were properly washed with detergent, rinsed with water, and finally rinsed with solvent to remove the interferences. The extraction of PAHs from the samples was reported elsewhere [10]. Briefly, using a graduated cylinder, 50 ml of each sample was measured into a 1-liter separatory funnel. A drop of concentrated H_2SO_4 was added to the sample in the separatory funnel to release the hydrocarbon components and 5ml of extraction solvent (n-Hexane) was also added. The sample was shaken vigorously for few minutes with periodic venting to release excess pressure and allowed to stand for 10 minutes to separate the organic layer (top layer) from the water phase (lower layer). The extraction was repeated two (2) times using fresh portions of solvent. The three solvent extracts were combined and transferred into a glass vial with a screw cap for further treatment [12].

2.5.2 Fractionation and concentration

Following the procedure of [13], the soluble organic matters were fractionated into aliphatic and aromatic fractions using a glass column packed with neutral alumina. 10 g of the alumina was packed into the column and properly cleaned with redistilled hexane. The extract was poured onto the alumina and was allowed to elute using the redistilled hexane to remove the aliphatic fractions into a precleaned 25 ml glass container. The aromatic fraction was recovered by using the mixture of hexane and dichloromethane in the ratio of 3:1. The aromatic fraction was concentrated to approximately 1.0 ml using a rotary evaporator. The resulting extract was stored in an organic-free precleaned glass vial with a screw cap for analysis. It was refrigerated at -4°C until analysis.

2.5.3 Instrumental analysis (USEPA 8270-C Method)

Gas Chromatography/ Mass spectrometer (GC/MS) analysis of the aromatic fractions was performed on a Hewlett-Packard model 6890 powered with Hewlett-Packard (HP) chemstation software. Separation was achieved using a column dimension of 30 m × 0.25 mm × 0.25 µm. The GC operating conditions were as follows: Temperature initially at 65 °C for 3 mins, increase from 65 °C to 320 °C at the rate of 10 °C min^{-1}. Helium was the carrier gas at 30.0 Psi. The sample was injected in the splitless mode with an injector temperature of 270 °C. The mass operator was operated in the selective ion mode (SIM) with a mass range of 128 – 202 amu (Group 1 -12) with a dwell time of 25 seconds. Data were acquired and processed with the chemstation software.

3 Results and discussion

3.1 Composition of PAHs in soil (at various depths) and water at different automobile repair workshops and control stations

As presented in Table 1, the soil samples obtained at Edem Udo automobile repair workshop (EU) had a mean value of PAHs concentration of 0.44 mg/kg(at 0-10 cm depth), 0.17 mg/kg(at 10-20 cm depth) and 0.35 mg/kg(at 20-30 cm depth). Figure 2 reveals that the most abundant individual PAHs found within EU was pyrene (1.10 mg/kg) at 0-10 cm depth, phenanthrene at 10-20 cm depth (0.78 mg/kg) and at 20-30 cm depth (1.03 mg/kg). In Table 2, the sum of Low Molecular Weight PAHs (LMW PAHs) were 1.06 mg/kg at 0-10 cm depth, 1.51 mg/kg at 10-20 cm depth and 1.21 mg/kg at 20-30 cm depth. The sum of these values was lower than the sum of High Molecular Weight PAHs (HMW PAHs). This may be attributed to the lower volatility of HMW PAHs due to their higher persistence in the soil environments when compared with LMW PAHs [14]. Most of the few ring PAHs were below detection level. Similarly, the mean concentration of water at EU was 1.19 mg/l (Table 3). As seen in Figure 2 and Table 3, the most abundant individual PAHs found in the water around this location was naphthalene (12.29 mg/l).

Table 1: Mean concentrations of PAHs (mg/kg) of soil samples at different sampling sites in the vicinity of automobile repair workshop and control site

Samples	Depths (cm)	PAHs Compounds (mg/kg)																	
		Nap	**Acy**	**Ace**	**Flu**	**Ant**	**Phe**	**Fla**	**Pyr**	**Chr**	**BaA**	**BbF**	**BkF**	**BaP**	**IcdP**	**DbA**	**BghiP**	**Mean**	**S.D.**
	0 – 10	0.28	-	-	-	0.37	0.41	-	1.10	0.26	0.24	0.68	0.30	0.29	0.48	-	0.44	0.44	0.25
EU	10 – 20	-	0.11	-	-	0.62	0.78	-	0.23	0.09	0.07	0.41	-	0.12	0.26	-	0.17	0.29	0.24
	20 – 30	-	0.24	-	-	-	1.03	-	0.15	-	0.13	0.72	-	0.09	-	-	0.12	0.35	0.37
	0 – 10	-	-	-	0.31	0.18	0.52	-	0.45	0.12	-	-	0.02	0.17	-	-	0.22	0.25	0.17
EIW	10 – 20	-	-	0.31	0.28	0.45	0.87	-	0.20	0.38	-	0.19	-	0.28	0.35	0.13	0.39	0.35	0.20
	20 – 30	-	-	-	0.19	0.06	-	-	0.34	0.11	-	-	0.08	0.09	-	0.05	-	0.13	0.10
	0 – 10	-	-	0.11	-	0.09	0.10	0.01	0.07	-	-	-	-	0.19	0.05	-	0.21	0.10	0.07
NK	10 – 20	-	-	-	-	0.28	0.24	-	0.42	0.36	-	-	-	-	0.12	-	-	0.28	0.12
	20 – 30	-	0.52	0.03	-	-	0.19	-	0.05	-	-	0.14	-	0.07	0.01	-	0.13	0.14	0.16
	0 – 10	0.01	-	-	0.18	0.38	0.36	0.01	-	-	0.13	0.22	-	0.18	0.03	-	0.12	0.16	0.13
GB	10 – 20	11.22	0.13	-	-	0.07	0.12		-	0.42	0.28	0.37	-	0.20	0.08	0.09	-	1.30	3.49
	20 – 30	2.51	0.31	-	-	0.07	-		-	0.49	-	0.19		0.11	0.07	-	0.16	0.49	0.83
	0 – 10	-	0.91	0.53	-	0.87	0.33		0.09	0.27	0.31	-	-	0.43	0.18	-	0.19	0.41	0.28
RCC	10 – 20	-	-	0.41	-	0.51	-		-	0.10	0.24	-	-	0.25	0.11	-	-	0.27	0.16
	20 – 30	-	0.73	0.42	-	0.26	0.09		0.01	0.06	-	-	-	-	0.12	-	0.18	0.23	0.24
	0 – 10	-	-	-	-	0.34	0.38	-	-	-	-	-	-	-	-	-	-	0.36	0.03
OPS (Control)	10 – 20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.00
	20 – 30	-	-	-	-	-	-	-	-	-	-	-	0.04	-	-	-	-	0.04	0.00

– :Below detectable limit (< 0.001), EU: Edem Udo, EIW: Etebi Idung Iwak, NK: Nkubia, GB: Grace Bill and RCC: RCC automobile repair workshop, OPS: Okon Primary School (Control)

Table 2: PAH concentrations in associated soil by number of rings and related PAH parameters

Samples	Depths (cm)	ΣLMW PAHs	ΣHMW PAHs	Σ16EPA PAHs	ΣPAHcarc	2-ring	3-ring	4-ring	5-ring	6-ring
EU	0 – 10	1.06	3.79	4.85	2.69	0.28	0.78	1.60	1.27	0.92
	10 – 20	1.51	1.35	2.86	1.12	-	1.51	0.39	0.53	0.43
	20 – 30	1.27	1.21	2.48	1.06	-	1.27	0.28	0.81	0.12
EIW	0 – 10	1.01	0.98	1.99	0.53	-	1.01	0.57	0.19	0.22
	10 – 20	1.91	1.92	3.83	1.72	-	1.91	0.58	0.60	0.74
	20 – 30	0.25	0.67	0.92	0.33	-	0.25	0.45	0.22	-
NK	0 – 10	0.30	0.53	0.83	0.45	-	0.30	0.08	0.19	0.26
	10 – 20	0.52	0.90	1.42	0.48	-	0.52	0.78	-	0.12
	20 – 30	0.74	0.40	1.14	0.35	-	0.74	0.05	0.21	0.14
GB	0 – 10	0.93	0.69	1.62	0.68	0.01	0.92	0.14	0.40	0.15
	10 – 20	11.54	1.44	12.98	1.44	11.22	0.32	0.70	0.66	0.08
	20 – 30	2.89	1.02	3.91	1.02	2.51	0.38	0.49	0.30	0.23
RCC	0 – 10	2.64	1.47	4.11	1.38	-	2.64	0.67	0.43	0.37
	10 – 20	0.92	0.70	1.62	0.70	-	0.92	0.34	0.25	0.11
	20 – 30	1.50	0.37	1.87	0.36	-	1.50	0.07	-	0.30
OPS(Control)	0 – 10	0.72	-	0.72	-	-	0.72	-	-	-
	10 – 20	-	-	-	-	-	-	-	-	-
	20 – 30	-	0.04	0.04	0.04	-	-	-	0.04	-

ΣLMW PAHs: Sum of low molecular weight PAHs; ΣHMW PAHs: sum of high molecular weight PAHs; Σ16EPA PAHs: sum of 16 EPA priority PAHs; ΣPAHcarc: sum of carcinogenic PAHs; 2-ring: sum of 2-ring PAHs; 3-ring: sum of 3-ring PAHs; 4-ring: sum of 4-ring PAHs; 5-ring: sum of 5-ring PAHs; 6-ring: sum of 6-ring PAHs, :Below detectable limit (< 0.001), EU: Edem Udo, EIW: Etebi Idung Iwak, NK: Nkubia, GB: Grace Bill and RCC: RCC automobile repair workshop, OPS: Okon Primary School (Control)

Table 3: Mean concentrations of PAHs in mg/l of water samples at different sampling sites in the vicinity of automobile repair workshop and control site

Sample Sites	PAHs Compounds (mg/l)																	
	Nap	Acy	Ace	Flu	Ant	Phe	Fla	Pyr	Chr	BaA	BbF	BkF	BaP	IcdP	DbA	BghiP	Mean	S.D.
EU	12.29	0.12	-	0.10	0.27	0.09	0.18	0.22	-	-	0.52	0.01	0.17	0.20	-	0.08	1.19	3.50
EIW	-	-	0.18	-	0.13	0.06	0.21	0.29	0.33	-	0.07	0.10	0.15	-	-	0.19	0.171	0.09
NK	0.75	-	-	0.20	-	-	0.45	0.27	-	-	0.09	-	0.13	0.07	-	0.15	0.26	0.23
GB	13.05	0.38	-	0.18	0.10	0.03	-	-	0.20	0.12	0.19	-	0.09	0.04	-	0.14	1.32	3.89
RCC	13.92	0.67	-	-	0.43	0.28	-	0.03	0.15	0.26	0.06	-	-	0.17	-	0.10	1.61	4.33
OPS (Control)	-	-	-	-	-	-	0.03	-	0.07	-	-	-	-	-	-	0.01	0.04	0.03

– :Below detectable limit (< 0.001); EU: Edem Udo; EIW: Etebi Idung Iwak; NK: Nkubia, GB: Grace Bill; RCC: RCC automobile repair workshop and OPS: Okon Primary School (Control)

Table 4: PAH concentrations in associated water by number of rings and related parameters

SAMPLE SITES	ΣLMW PAHs	ΣHMW PAHs	Σ16EPA PAHs	ΣPAHcarc	2-ring	3-ring	4-ring	5-ring	6-ring
EU	12.87	1.38	14.25	0.98	12.29	0.58	0.40	0.70	0.28
EIW	0.37	1.34	1.71	0.84	-	0.37	0.83	0.32	0.19
NK	0.95	1.16	2.11	0.44	0.75	0.20	0.72	0.22	0.22
GB	13.74	0.78	14.52	0.78	13.05	0.69	0.32	0.28	0.18
RCC	15.30	0.77	16.07	0.74	13.92	1.38	0.44	0.06	0.27
OPS (Control)	-	0.11	0.11	0.08	-	-	0.10	-	0.01

ΣLMW PAHs: Sum of low molecular weight PAHs: ΣHMW PAHs: sum of high molecular weight PAHs; Σ16EPA PAHs: sum of 16 EPA priority PAHs; ΣPAHcarc: sum of carcinogenic PAHs; 2-ring: sum of 2-ring PAHs; 3-ring: sum of 3-ring PAHs; 4-ring: sum of 4-ring PAHs; 5-ring: sum of 5-ring PAHs; 6-ring: sum of 6-ring PAHs, – :Below detectable limit (< 0.001); EU: Edem Udo; EIW: Etebi Idung Iwak; NK: Nkubia, GB: Grace Bill; RCC: RCC automobile repair workshop and OPS: Okon Primary School (Control)

The PAHs with the lowest concentration were Benzo(k)fluoranthene (0.01 mg/l). The sum of LMW PAHs was 12.87 mg/l, a value which was higher than HMW PAHs (1.38 mg/l) as observed in Table 4. Acenapthalene, chrysene, benzo(a)anthracene, and dibenzo(a, h)anthracene were below the detectable limit in the water sample.

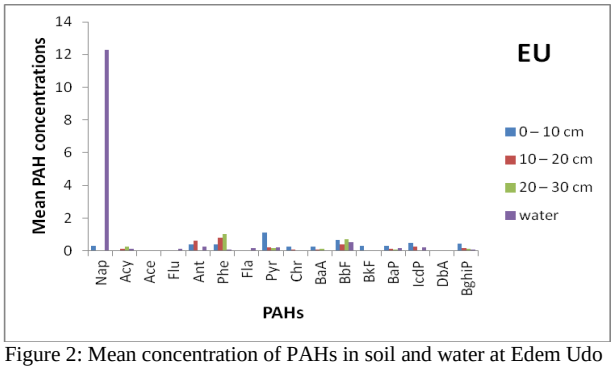

Figure 2: Mean concentration of PAHs in soil and water at Edem Udo

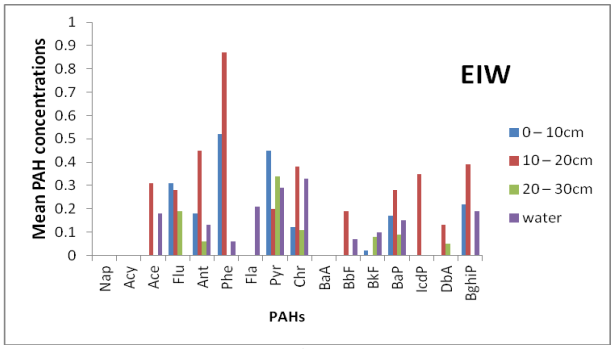

Figure 3: Mean concentration of PAHs in soil and water at Etebi Idung Iwak

The situation in the soil sample obtained from Etebi Idung Iwak automobile repair workshop (EIW) was also similar to that of the EU. The mean values of PAHs concentration in soil were 0.25 mg/kg at 0-10 cm, 0.35 mg/kg at 10-20 cm and 0.13 mg/kg at 20-30 cm (Table 1). Figure 3 reveals that the most abundant individual PAHs found within the sampling site was phenanthrene at 0-10 cm (0.52 mg/kg) and 10-20 cm (0.87 mg/kg) and pyrene at 20-30 cm (0.34 mg/kg). As seen in Table 2, the sum of LMW PAHs was lower than the sum of HMW PAHs at 10-20 cm depth (1.91 mg/kg) and 20-30 cm depth (0.25 mg/kg). The reverse was the situation at 0-10 cm depth, were the sum of LMW PAHs (1.01 mg/kg) was higher than the sum of HMW PAHs (0.98 mg/kg). Around Etebi Idung Iwak automobile repair workshop environment, Table 3 shows that the mean concentration of studied PAHs in water samples was 0.17 mg/l. The most abundant individual PAHs found around this vicinity were chrysene (0.33 mg/l). As seen in Figure 3 and Table 3, the individual PAHs with the lowest concentration was phenanthrene (0.06 mg/l). Acenapthylene and dibenzo(a,h)anthracene were below the detectable limit in the water sample. In Table 4, it is seen that the sum of LMW PAHs (0.37 mg/l) was lower than the sum of HMW PAHs (1.34 mg/l).

The situation at the Nkubia location (NK) was also similar to that of the already discussed locations. The mean values of PAHs concentration in soil were 0.10 mg/kg at (0-10 cm) depth, 0.28 mg/kg at 10-20 cm depth and 0.14 mg/kg at 20-30 cm (Table 1). The most abundant individual PAHs in this study site was benzo(ghi)perylene (0.21 mg/kg) at 0.10 cm depth, pyrene (0.42 mg/kg) at 10-20cm depth and acenapthylene (0.52 mg/kg) at 20-30 cm depth (Figure 4). The sums of LMW PAHs were lower than the sum of HMW PAHs except at 20-30 cm depth where the sum of LMW PAHs was higher than the sum of HMW PAHs (Table 2).

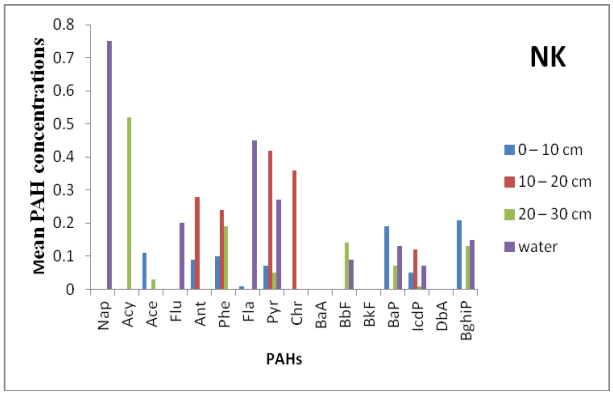

Figure 4: Mean concentration of PAHs in soil and water at Nkubia

From figure 4 and Table 3, we see that the mean concentration of studied PAHs in water samples collected around NK was similar to the situation at EU and EIW locations. The mean concentration of the studied PAHs in water samples was 0.26 mg/l. The most abundant individual PAHs found in this studied site was naphthalene (0.75 mg/l). The PAHs with the lowest mean concentration was indeno(1,2,3-cd)pyrene (0.07 mg/l). As seen in Table 4, the sum of LMW PAHs (0.95 mg/l) was lower than the sum of HMW PAHs (1.16 mg/l). As in the case of EIW, acenapthylene and dibenzo(a,h)anthracene were below the detectable limit in the water samples.

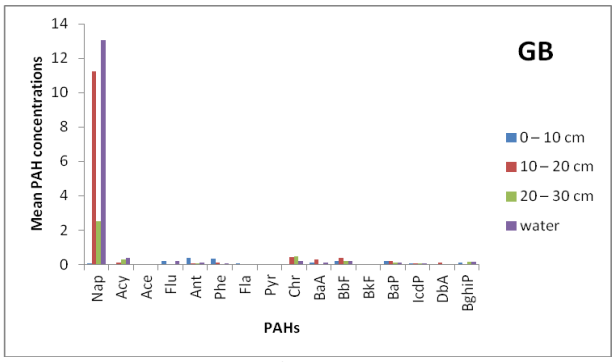

Figure 5: Mean concentration of PAHs in soil and water at Grace Bill

As presented in Table 1, Grace Bill automobile repair workshop (GB) mean values of PAHs concentration in soil were 0.16 mg/kg at 0-10 cm depth, 1.30 mg/kg at 10-20cm depth and 0.49 mg/kg at 20-30 cm depth. The most abundant individual PAHs in this sampling site were anthracene (0.38 mg/kg) at 0-10 cm depth and naphthalene 11.22 mg/kg and 2.51 mg/kg at 10-20 cm and 20-30 cm depth respectively (Figure 5). In this study location, the sum of LMW PAHs was higher than the sum of HMW PAHs at all soil depths (Table 2). Around GB, the mean concentration of the studied PAHs in water samples was 1.32 mg/l (Table 3). From Figure 5 and Table 3, we see that the most abundant individual PAHs obtained in this location was naphthalene (13.05 mg/l). The individual PAH with the lowest concentration in this location was phenanthrene (0.03 mg/l). Acenapthalene, fluoranthene,

benzo(k)fluoranthene, and dibenzo(a,h)anthracene were below the detectable limit in the samples. As seen in Table 4, the sum of HMW PAHs (0.78 mg/l) was lower than the sum of LMW PAHs (13.74 mg/l).

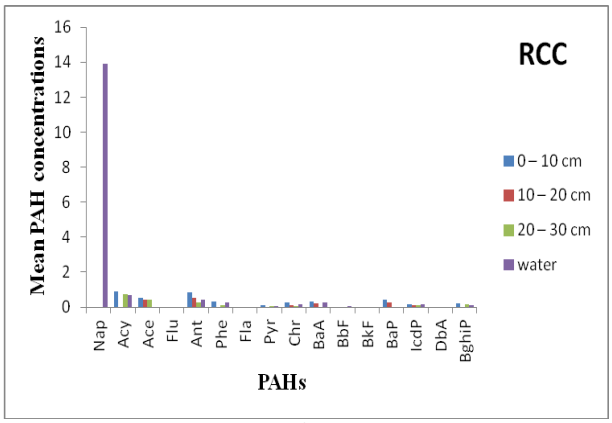

Figure 6: Mean concentration of PAHs in soil and water at RCC

In the soil samples collected at RCC automobile repair workshop (RCC), the mean values of PAHs concentration at 0-10 cm depth was 0.41 mg/kg, 0.27 mg/kg at 10-20 cm depth and 0.23 mg/kg at 20-30 cm. As seen in Figure 6, the most abundant individual PAHs found within RCC were acenaphthene (0.91 mg/kg) at 0-10 cm depth and (0.73 mg/kg at 20-30 cm depth) and anthracene (0.51 mg/kg) at 10-20 cm depth. The sum of LMW PAHs was higher than the sum of HMW PAHs at all levels (Table 2). Around RCC, the mean concentration of studied PAHs in water samples was 1.61 mg/l (Table 4). Benzo(k)fluoranthene and dibenzo(a,h)anthracene were below the detection limit in the sample. The most abundant individual PAH in this location was naphthalene. This was a similar situation at EU, NK, and GB locations. The individual PAH as observed in Table 3 with the lowest concentration was pyrene (0.03 mg/l). The sum of LMW PAHs (15.30 mg/l) was higher than the sum of HMW PAHs (0.77 mg/l) as seen in Table 4. This might be due to their affinity to be adsorbed on the dissolved organic matter [15].

3.2 PAHs distribution pattern in the study area

As presented in Table 2, PAHs levels in Eket were high at some specific locations which are: GB(12.98 mg/kg) and EU(4.85 mg/kg). This shows that the major source of PAHs contamination is mostly pointed sources. GB and EU are long-standing (> 10yrs) repair yards and their activities are more intense than other mechanic workshops. All the various PAHs analyzed in this study were found at these locations except acenapthylene which was not found at all in the soil sample. Most of the PAHs were not found in soil samples obtained at the control station except anthracene, phenanthrene, and benzo(k)fluoranthene. This is because there were little or no activities around the control station except for a residential purpose. PAHs present in the soil samples did not follow a regular pattern with the depth of the soil. In all the soil samples, the three-ring PAHs had the highest concentration, next to the two-ring PAHs. The 6-ring PAHs had the lowest concentration. The Σ16 EPA PAHs had a concentration range of 0.83 mg/kg to 12.98 mg/kg (Table 2). According to the European Commission classification system of soil contamination Σ16 EPA PAHs < 0.20 mg/kg show no contamination, 0.20 – 0.60 mg/kg corresponds to weak contamination, 0.60 – 1.00 mg/kg corresponds to weak moderate contamination and >1.0 mg/kg corresponds to heavy contamination [16]. Following this classification, it can be said that the soil in the Eket metropolis is moderate to heavily contaminated. Also, according to the WHO critical level recommendation of 4 mg/kg, some of the areas are considered to be contaminated by PAHs such as Edem Udo, Grace Bill, and RCC repair yards.

In the water samples, the sum of 16 US EPA priority PAHs (Σ16 EPA PAHs) understudy was high at some specific locations such as EU (14.25 mg/l), GB (14.52 mg/l), and RCC (16.07 mg/l) as seen in Table 4. This was similar to the situation in the soil samples in the same location, indicating that the PAHs may have been as a result of leaching from the soil (due to the automobile repair activities and the soil texture) into the underground water [10]. Also, the automobile repair workshops have been in operation there for quite a long time leading to a major source of PAH contamination. As seen in table 3, dibenzo(a,h) anthracene was not detected in any of the water samples showing that this PAH was not transferred from the soil to the underground water because of its low concentration in the soil samples. This was similar to the result observed by [17] in their research on human health and ecological risk assessment of 16 PAHs in drinking source water from a large mixed-use reservoir. Most of the PAHs were not present in water samples obtained at the control station except fluoranthene, chrysene, and benzo(ghi)perylene which was in very low concentrations. This is because there were little or no activities around the control station. The two-ring PAHs had the highest concentration in the entire water samples while the five- and six-ring PAHs were the lowest in concentration. 2-ring PAHs were not detected in water samples obtained from EIW (Table 4). The distribution of PAHs concentration based on the number of rings followed this order: 2-ring > 3-ring >4-ring >5-ring > 6-ring. The probable source of these compounds is organic matter combustion at low temperatures [18]. Relatively high concentration in comparison to HMW PAHs can be explained by the relative solubility of the PAHs. The pattern of concentration has been seen by other research such as [19] and [20].

3.3 Estimation of carcinogenic potency of the soil and water

The PAHs carcinogenic potency was estimated by calculating the concentration of individual carcinogenic PAHs in terms of benzo(a)pyrene equivalent (BaPeq) which is represented as follows (Eq. 1):

$$\text{Total BaPeq} = \Sigma_i (C_i * TEF_i) \quad \text{(Eq. 1)}$$

where C_i is the concentration of individual PAHs and TEF_i is the toxic equivalent factor relative to benzo(a)pyrene [21]. The TEQ of individual PAHs was calculated based on the toxic equivalency factor (TEF) values proposed by [22] as shown in Table 5. International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (US EPA) reported Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene(BaP), Indeno(1,2,3-cd)pyrene (IcdP), Dibenzo(a,h)anthracene (DbA) and Benzo(ghi)perylene (BghiP) as possible human carcinogens. These possible carcinogens were detected in the samples. Most of the carcinogenic PAHs were absent at the Control station except Benzo(k)fluoranthene (0.04 mg/kg). The highest concentration of carcinogenic PAHs in soil was 4.87 mg/kg and was recorded in soil from the Edem Udo automobile repair workshop while the lowest concentration was 1.28 mg/kg recorded in the soil from the Nkubia Street automobile repair workshop.

Table 5: Carcinogenic potency of PAHs in soil and water within the vicinity of automobile repair workshop and control site in Eket Metropolis, Akwa Ibom State

CARCINOGENIC PAHS	LEVEL OF CARCINOGENIC PAHs						TEF	BaPeq					
	EU	EIW	NK	GB	RCC	OPS		EU	EIW	NK	GB	RCC	OPS
	Soil							**Soil**					
Chrysene	0.35	0.61	0.36	0.91	0.43	-	0.01	0.0035	0.0061	0.0036	0.0091	0.0043	0.0000
Benzo(a)anthracene	0.44	0.00	0.00	0.41	0.55	-	0.1	0.0440	0.0000	0.0000	0.0410	0.0550	0.0000
Benzo(b)fluoranthene	1.81	0..19	0.14	0.78	0.00	-	0.1	0.1810	0.0190	0.0140	0.0780	0.0000	0.0000
Benzo(k)fluoranthene	0.30	0.10	0.00	0.00	0.00	0.04	0.1	0.0300	0.0100	0.0000	0.0000	0.0000	0.0040
Benzo(a)pyrene	0.50	0.54	0.26	0.49	0.68	-	1	0.5000	0.5400	0.2600	0.4900	0.6800	0.0000
Indeno(1,2,3-cd)pyrene	0.74	0.35	0.18	0.18	0.41	-	0.1	0.0740	0.0350	0.0180	0.0180	0.0410	0.0000
dibenzo(a,h)anthracene	0.00	0.18	0.00	0.09	0.00	-	1	0.0000	0.1800	0.0000	0.0900	0.0000	0.0000
Benzo(ghi)perylene	0.73	0.61	0.34	0.28	0.37	-	0.01	0.0073	0.0061	0.0034	0.0028	0.0037	0.0000
TOTAL								**0.8398**	**0.7962**	**0.2990**	**0.7289**	**0.7840**	**0.0040**
	Water							**Water**					
Chrysene	-	0.33	-	0.20	0.15	0.07	0.01	0.0000	0.0033	0.0000	0.0020	0.0015	0.0007
Benzo(a)anthracene	-	-	-	0.12	0.26	-	0.1	0.0000	0.0000	0.0000	0.0120	0.0260	0.0000
Benzo(b)fluoranthene	0.52	0.07	0.09	0.19	0.06	-	0.1	0.0520	0.0070	0.0190	0.0120	0.0060	0.0000
Benzo(k)fluoranthene	0.01	0.1	-	-	-	-	0.1	0.0010	0.0100	0.0000	0.0000	0.0000	0.0000
Benzo(a)pyrene	0.17	0.15	0.13	0.09	-	-	1	0.1700	0.1500	0.1300	0.0900	0.0000	0.0000
Indeno(1,2,3-cd)pyrene	0.20	-	0.07	0.04	0.17	-	0.1	0.0200	0.0000	0.0070	0.0040	0.0170	0.0000
dibenzo(a,h)anthracene	-	-	-	-	-	-	1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Benzo(ghi)perylene	0.08	0.19	0.15	0.14	0.10	0.01	0.01	0.0008	0.0019	0.0015	0.0014	0.0010	0.0001
TOTAL								**0.2438**	**0.1722**	**0.1575**	**0.1214**	**0.0515**	**0.0008**

TEF: toxic equivalent factor; **BaPeq:** benzo(a)pyrene equivalent; -: not detected; EU: Edem Udo; EIW: Etebi Idung Iwak; NK: Nkubia, GB: Grace Bill; RCC: RCC automobile repair workshop and OPS: Okon Primary School (Control)

Benzo(a)pyrene was detected in all the samples in both rainy and dry seasons thereby making the use of the soil very risky due to its carcinogenic potency. The calculated total BaPeq values in this study at different sampling sites varied from 0.2990 mg/kg to 0.8398 mg/kg. EU exhibited the highest total BaPeq values(0.8398 mg/kg) while NK recorded the lowest total BaPeq value (0.2990 mg/kg) (Table 5). This is due to the level of activities going on at the different automobile repair workshops and the number of years of automobile repair activities. In the water samples, Benzo(a)pyrene was also detected in almost all the water samples except the sample collected around the RCC automobile repair workshop. Water samples collected around the EU automobile repair workshop had the highest concentration of total carcinogenic PAHs (ΣPAHcarc) of 0.98 mg/l (Table 4). It shows serious health risks for the human population consuming this water. As seen in Table 5, benzo(a)pyrene equivalent concentration was in the range 0.0515 mg/l to 0.2438 mg/l. Water samples collected around the EU automobile repair workshop had the highest value of Benzo(a)pyrene equivalent (0.2438 mg/l) while GB recorded the lowest total BaPeq value (Table 5). This was similar to the situation in the soil samples analyzed in the same location (EU). This value was attributed to the type of oil used and the level of activities carried out around the repair vicinity.

3.4 PAHs source identification

It is important to identify the origin and potential sources of PAHs in the environment to assess the environmental risk. The anthropogenic release of PAHs can be attributed to petrogenic and pyrogenic origins. The pyrogenic, petrogenic, and pyrogenic sources of PAHs were also assessed using the diagnostic ratios including Ant/(Ant + Phe), Fla/(Fla + Pyr), BaA/(BaA + Chr), and IcdP/(IcdP + BghiP) to quantitatively distinguish anthropogenic PAHs inputs. PAHs diagnostic ratio was calculated from the readings and the result is shown in Table 6. From Table 6, diagnosis of the PAHs ratios showed that Ant/(Ant + Phe) for soil samples ranged from 0.30-0.74. This shows that PAHs from here are of pyrogenic origin. The ratio Fla/(Fla + Pyr) was not available in almost all the samples except in soil within NK which had a value of 0.13, a value showing petrogenic origin. The BaA/(BaA + Chr) ratio had a range from 0.40-0.62 showing that the PAHs present in the soil was of pyrogenic origin. The ratio IcdP/(IcdP + BghiP) had a range of 0.13-0.56, indicating that the PAHs present in the soil are from mixed sources (petrogenic, pyrogenic, and phytogenic sources). In the water samples as seen in Table 6, the ratio Ant/(Ant + Phe) for water samples showed a range of 0.61-0.77. This shows that PAHs in the water samples were of pyrogenic origin. Using this ratio, the source of PAH in the water sample collected from NK was not possible to be identified. Considering the ratio Fla/(Fla + Pyr), the range was from 0.42-0.63 indicating mixed sources(pyrogenic, petrogenic, and phytogenic). GB and RCC had no value judgment as to where the source of PAHs was from. The BaA/(BaA + Chr) ratio had a range from 0.60-0.63, showing that the PAHs present in the water was of pyrogenic origin. It was not possible to identify the source of PAH in a water sample collected from EU, EIW, and NK using this ratio. The ratio IcdP/(IcdP + BghiP) had a range of 0.22-0.71, indicating that the PAHs present in the water is from pyrogenic and phytogenic sources. It was not possible to identify the source of PAH in the water sample collected from EIW using this ratio. It is noticed that there are many sources identified for a particular location. The condition that could be responsible for the many sources especially in soil samples is the run-off from rainwater which could have washed several PAHs from various sources thereby giving conflicting PAHs ratios from source determination [23].

3.5 Correlation between the PAHs in soil and PAHs in water within and around automobile repair workshop

The correlation coefficient was calculated using Microsoft Excel 2010 software. It was important to calculate the correlation coefficient (r) to deduce whether there is a possible relationship between the PAHs present in the soil and the PAHs present in the underground water to know if they originate from the same source.

Table 6: PAHs diagnostic ratios for soil samples and water samples

SITES	PAHs diagnostic ratios for soil and water samples							
	Ant/(Ant+Phe)		Fla/(Fla+Pyr)		BaA/(BaA+Chr)		IcdP/(IcdP+BghiP)	
	Soil	Water	Soil	Water	Soil	Water	Soil	Water
EU	0.46	0.75	nd	0.45	0.46	nd	0.56	0.71
EIW	0.30	0.68	nd	0.42	nd	nd	0.47	nd
NK	0.51	nd	0.13	0.63	nd	nd	0.13	0.32
GB	0.44	0.77	nd	nd	0.40	0.60	0.25	0.22
RCC	0.74	0.61	nd	nd	0.62	0.63	0.45	0.63

Ant; Anthracene, **Phe;** Phenanthrene, **Fla;** Fluoranthene, **Pyr;** Pyrene, **BaA;** Benzo[a]Anthracene, **Chr;** Chrysene, **IcdP;** Indeno(1,2,3-cd)Pyrene, **BghiP;** Benzo(ghi)Peryene, **nd**: cannot be determined because of the zero value of the nominator and/or denominator, EU: Edem Udo; EIW: Etebi Idung Iwak; NK: Nkubia, GB: Grace Bill; RCC: RCC automobile repair workshop and OPS: Okon Primary School (Control).

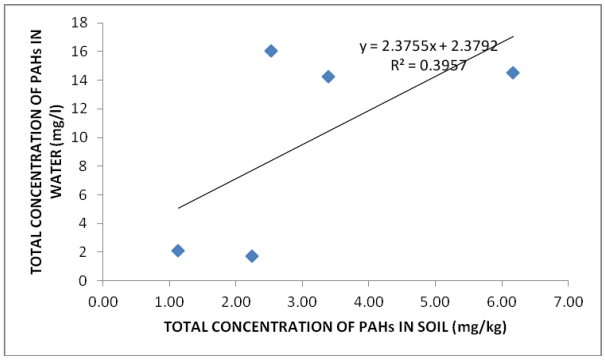

Figure 7: Correlation between the total PAH concentration in soil and water

Using scattered plots and determination of Pearson's product-moment correlation coefficient as seen in Figure 7, there was a positive correlation between PAHs in soil and PAHs in the underground water around the soil environment (r = 0.40). This indicates that there is a direct relationship between the PAHs in the soil within the automobile repair yard and the underground water around the automobile repair environment. Also, it is possible that the PAHs in the soil percolated into the underground water to contaminate it.

4 Conclusion

In this study, the PAHs distribution profile in soils within automobile repair workshops and underground water around its vicinity indicated moderate to heavy contamination with PAHs. The value of the total BaPeq for the soil samples indicated a moderate carcinogenic burden. The calculated values obtained from diagnostic ratios and individual PAHs correlation indicated that the PAHs in this study were from both pyrogenic and petrogenic sources. It can be concluded that automobile repair activities affected the soil contamination with PAHs. The correlation between total PAH concentration in soil and water indicated that the PAHs in water were contributed by the PAHs in soil. It can be concluded that automobile repair activity has a moderate effect on the soil as well as the underground water around it. Therefore boreholes should be sited distance away from the automobile repair yards to enable their suitability for domestic, irrigation, recreational, and industrial usage.

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Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language. Also, all procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards. All procedures performed in this study involving animals were following the ethical standards of the institution or practice at which the studies were conducted.

Ethical issues

Conflict of interest: On behalf of all authors, the corresponding author states that there is no conflict of interest.

Authors' contributions

Akanimo N. Ekanem performed the literature review, experimental design, analyzed, prepared the manuscript text, and compiled the data. Bassey S. Okori and Godwin J. Udo performed a brief literature review, interpreted the data and manuscript edition.

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